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Comment on: 'A simple cryogenic method for efficient measurement of triple oxygen isotopes in silicates' by Ghoshmaulik et al.

Journal Item

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LETTER TO THE EDITOR

Comment on: 'A simple cryogenic method for efficient measurement of triple oxygen isotopes in silicates' by Ghoshmaulik et al. (Rapid Commun Mass Spectrom. 2020;34(18):e8833)

In a recent article in this journal, Ghoshmaulik et al.¹ described technical modifications to a long-established laser-assisted fluorination procedure for extracting and purifying molecular oxygen from silicates, prior to triple-isotope ratio analysis. Although the reported respective measurement precisions for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values, at 0.040‰ and 0.080‰, are identical to those reported more than 20 years ago,² using a similar (but not identical) system and protocol, the very tight coupling of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ measurement errors in the new method permits the determination of $\Delta^{17}\text{O}$ values* to a precision of 4 ppm, or even less. All precision values discussed herein refer to one standard deviation (σ). The description of how Ghoshmaulik et al.¹ achieved such precise $\Delta^{17}\text{O}$ values is a welcome contribution to the increasing number of reports quantifying small but distinctive variations between the relative abundances of ^{17}O and ^{18}O in terrestrial silicate rocks and minerals.

Distinct from $\Delta^{17}\text{O}$ precision – which is independent of calibration of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data to any particular reference material – is the corresponding accuracy of the data on a designated scale. Conversion of the empirical $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data, as reported relative to a 'working standard' O_2 , into the corresponding values relative to the Vienna Standard Mean Ocean Water (VSMOW) reference, with a degree of accuracy commensurate with the $\Delta^{17}\text{O}$ precision, is challenging. The difficulty is, at least in part, compounded by the use of a water reference for the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ scales, whereas silicates and waters require different fluorination procedures for the extraction of molecular oxygen, the analyte gas used for the triple-isotope ratio measurements. Furthermore, few laboratories have the capability to make such measurements on silicates and on waters. Even those that do, which (in principle, at least) enables accurate calibration of the 'working standard' O_2 to VSMOW, and any

instrument-related compression of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ scales to be quantified from measurements of the Standard Light Antarctic Precipitation (SLAP) reference, for which $\Delta^{17}\text{O}$ is defined³ to be zero for the VSMOW-SLAP scale, may nevertheless (as discussed below) report differing $\Delta^{17}\text{O}$ values for commonly used silicate standards such as San Carlos olivine, UWG-2 garnet and NBS 28 quartz. This is despite using the same definition for $\Delta^{17}\text{O}$.

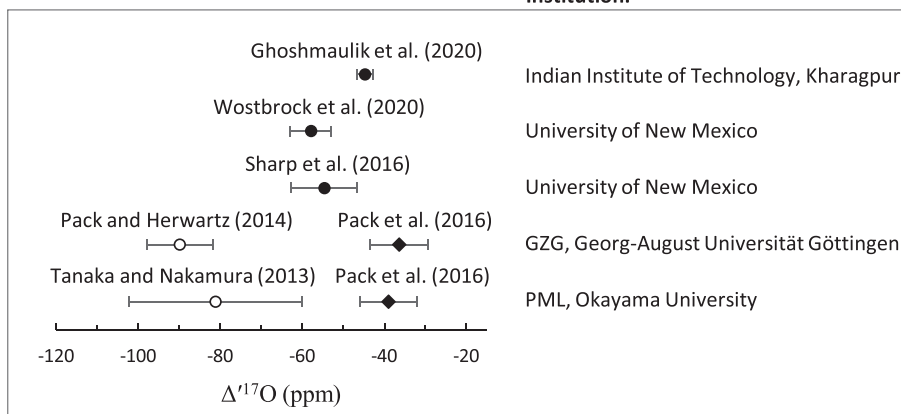
Ghoshmaulik et al.¹ calibrated their laboratory 'working standard' O_2 using replicate measurements of oxygen extracted from NBS 28 quartz, in conjunction with the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values for NBS 28 reported recently by Wostbrock et al.⁴ Whereas that is a legitimate approach, we note that there is currently no consensus on those values. As far as we are aware, only three laboratories have (to date) reported $\Delta^{17}\text{O}$ values of one or more silicate standards to a precision of <10 ppm and also made similarly high-precision measurements of reference waters VSMOW and SLAP. The first such report was by Pack et al.⁵ in 2016 and described an inter-laboratory comparison of the $\Delta^{17}\text{O}$ value of San Carlos olivine as performed at Georg-August Universität Göttingen, Germany, and at the Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry, Okayama University, Japan. Remarkably close agreement was obtained, with the former institution reporting $\Delta^{17}\text{O} = -36 \pm 7$ ppm whereas the latter obtained -39 ± 7 ppm. Those data were calibrated to the VSMOW-SLAP scale. Whereas we recognise that the consistency of the $\Delta^{17}\text{O}$ data obtained independently in this inter-laboratory comparison does not validate its accuracy, it is to date the only instance of such agreement. Four weeks after publication of the Pack et al.⁵ paper, Sharp et al.⁶ published their finding that San Carlos olivine, as measured at the University of New Mexico, USA, is characterised by a more negative $\Delta^{17}\text{O}$ value, -54 ± 8 ppm. Although not corrected for measurements of SLAP, doing so (from data on SLAP reported in the same paper) reduces the $\Delta^{17}\text{O}$ value by only 1 ppm.

Regrettably, when comparing their own $\Delta^{17}\text{O}$ determination of San Carlos olivine with published, high-precision values,

* $\Delta^{17}\text{O}$ is defined as $\ln(1 + \delta^{17}\text{O}) - \lambda_{\text{RL}} \ln(1 + \delta^{18}\text{O}) - \gamma_{\text{RL}}$ and is a measure of the $\ln(1 + \delta^{17}\text{O})$ deviation of an individual sample from an assigned reference line (RL), of slope λ_{RL} , on a plot of $\ln(1 + \delta^{17}\text{O})$ versus $\ln(1 + \delta^{18}\text{O})$. The ordinate intercept of the reference line is denoted by γ_{RL} and is usually set to zero. As in many recent articles, λ_{RL} is assigned a value of 0.528 by Ghoshmaulik et al.¹

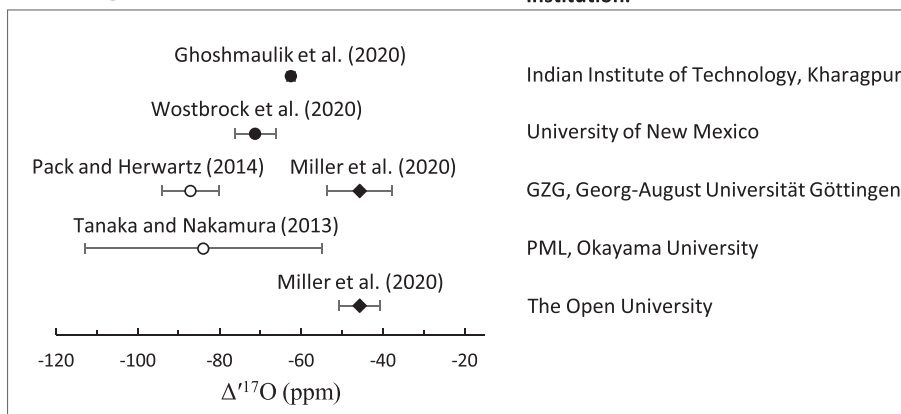
San Carlos olivine

Institution:



UWG-2 garnet

Institution:



NBS 28 quartz

Institution:

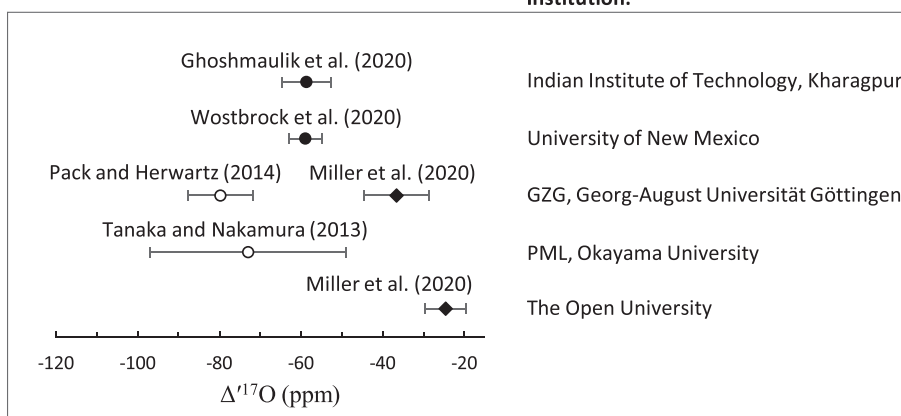


FIGURE 1 Comparison of the $\Delta^{17}\text{O}$ values of widely used silicate standards San Carlos olivine, UWG-2 garnet and NBS 28 quartz, as determined from high-precision measurements in different laboratories. Filled circles (●) indicate recent measurements reported in Table 2 of Ghoshmaulik et al.¹ Open circles (○) indicate results also reported in the same table but which have since been acknowledged to have been incorrectly calibrated to VSMOW. Filled diamonds (◆) indicate data which were not mentioned by Ghoshmaulik et al.¹ but should have been cited in their paper for comparison, we suggest. GZG refers to Geowissenschaftliches Zentrum; PML refers to the Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry, which is located within the Institute of Planetary Materials at Okayama University. In Pack et al.,⁵ the Institute is referred to by its earlier name of the Institute for Study of the Earth's Interior (ISEI). $\Delta^{17}\text{O}$ data reported by Tanaka and Nakamura⁸ have been recalculated using a slope value of 0.528 instead of 0.527 as in that publication

Ghoshmaulik et al.¹ did not mention the inter-laboratory comparison reported by Pack et al.⁵ Instead, in Table 2 of their article, they compared their measurements with those reported in two earlier studies^{7,8} which Pack et al.⁵ had already noted were based on erroneous calibrations to VSMOW (resulting in $\Delta^{17}\text{O}$ values that were ~50 ppm too negative in one case⁷ and ~42 ppm too negative in the other^{8,†}). Ghoshmaulik et al.¹ also compared their $\Delta^{17}\text{O}$ data with measurements reported by Levin et al.,⁹ the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ data

of which were not originally calibrated to VSMOW. Furthermore, for San Carlos olivine in particular, the $\Delta^{17}\text{O}$ value reported by Levin et al.⁹ was of much lower precision (by a factor of nine) than that in the investigation by Pack et al.⁵ The article by Ghoshmaulik et al.¹ therefore misrepresents the current state of knowledge about the $\Delta^{17}\text{O}$ value of San Carlos olivine. There is currently a difference of ~16–20 ppm between values⁵ obtained at Georg-August Universität Göttingen and at Okayama University, on the one hand, and those obtained^{4,6} at the University of New Mexico. The reason for the discrepancy is currently not known. We compare the data from these recent studies in Figure 1, which (for completeness) also

[†]with $\Delta^{17}\text{O}$ recalculated from Tanaka and Nakamura⁸ using λ_{RL} assigned as 0.528 instead of 0.527.


includes the 'superseded' data that Ghoshmaulik et al¹ cite in Table 2 of their paper. Additional calibrations of their 'working standard' O₂ performed by Ghoshmaulik et al,¹ using canisters of high-purity O₂, were also anchored to measurements reported by Wostbrock et al⁴ and therefore do not provide an independent validation.

In a study published just before that of Wostbrock et al,⁴ an inter-laboratory investigation¹⁰ involving Georg-August Universität Göttingen and The Open University, UK, reported that (as found at both institutions) the $\Delta^{17}\text{O}$ value of UWG-2 garnet is 8 ppm lower than that of San Carlos olivine. The respective precisions were in the range 5–9 ppm and calibration to VSMOW was based on measurements of San Carlos olivine reported by Pack et al.⁵ In contrast, measurements⁴ at the University of New Mexico suggest that UWG-2 has a $\Delta^{17}\text{O}$ value 13 ppm lower (-71 ± 5) than that of San Carlos olivine (-58 ± 5).

Because quartz is more difficult to fluorinate completely by laser heating in the presence of BrF₅ than is San Carlos olivine or UWG-2 garnet,^{8,11} the latter two silicates are more commonly used for calibration purposes. We note that, with normalising their data to the NBS 28 measurements of Wostbrock et al,⁴ Ghoshmaulik et al¹ obtained $\Delta^{17}\text{O}$ results for San Carlos olivine and UWG-2 garnet that differ from those reported by Wostbrock et al,⁴ with the discrepancies being 13 ppm and 9 ppm, respectively. It is interesting to note that, in the recent investigation¹⁰ involving Georg-August Universität Göttingen and The Open University, excellent inter-laboratory agreement was obtained on the $\Delta^{17}\text{O}$ values of two proposed silicate standards that differ in $\delta^{18}\text{O}$ value by more than 59‰, yet the two institutions did not obtain agreement on the $\Delta^{17}\text{O}$ value of NBS 28; a discrepancy of 12 ppm was reported. We suggest that this is in accord with NBS 28 not being optimal for $\Delta^{17}\text{O}$ calibration, unless a fluorination protocol specific to quartz is adopted.^{8,11}

Ghoshmaulik et al¹ suggested that their cryogenic purification protocol efficiently removes NF₃ contaminants from oxygen gas produced by laser fluorination of silicates, without the need to use gas chromatography to isolate the oxygen from other components that may be present. In the two inter-laboratory investigations reported above,^{5,10} however, gas chromatographic purification of the oxygen was used at one of the institutions, but not at the other. Yet very good agreement was obtained for the $\Delta^{17}\text{O}$ value of San Carlos olivine in the one study⁵ that measured only that silicate standard, and for three of the four silicates (all except NBS 28) investigated in the other study.¹⁰ Even without implementing the procedural improvements suggested by Ghoshmaulik et al,¹ therefore, a gas chromatographic purification step does not seem to be essential to obtaining $\Delta^{17}\text{O}$ values of high precision and reproducibility. Furthermore, we have not found NF₃ to be detectable in the oxygen extracted from silicates such as San Carlos olivine, UWG-2 garnet and NBS 28 quartz. In our experience, it is usually when analysing samples of specific types of meteorites (notably, carbonaceous chondrites) that NF₃ is likely to be produced during the silicate fluorination step. The accuracy and precision of $\Delta^{17}\text{O}$ determinations are probably controlled

principally by the efficiency of molecular oxygen adsorption and desorption to/from the cryo-cooled zeolite pellets, assuming that the oxygen 'blank' level associated with the complete extraction and purification procedures is shown to be of negligible magnitude and that the BrF₅ used for the fluorination step is of high purity. Consequently, details of the cryogenic transfer arrangement and protocol are critical, as is the complete removal of volatile contaminants from the zeolite pellets between the analysis of successive samples. The procedure described by Ghoshmaulik et al¹ is therefore a welcome contribution, which offers the potential for improving the precision of silicate $\Delta^{17}\text{O}$ determinations. The challenge remains, however, to understand why different laboratories which calibrate oxygen triple-isotope data directly to VSMOW or to the VSMOW-SLAP scale do not obtain consensus on the $\Delta^{17}\text{O}$ values of San Carlos olivine, UWG-2 garnet and NBS 28 quartz.

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